IT IS CLAIMED:

1. A catalytic organometallic composition, comprising a central metal atom selected from the group consisting of molybdenum, tungsten, and chromium, and coordinated thereto, a chiral ligand L^1 comprising:

(i) a chiral component derived from a chiral diamine, diol, or amino alcohol, said component having first and second chiral centers, each substituted with a group X selected from -O- or -NR-, where R is hydrogen or lower alkyl, and, linked to each said group X,

(ii) a binding group Cy_N comprising a heterocyclic group having a ring nitrogen atom effective to bind to said central metal atom, wherein said heterocyclic group is optionally substituted with one or more groups selected from alkyl, alkenyl, aryl, aralkyl, alkoxy, aryloxy, acyl, acyloxy, amide, tertiary amine, nitro, or halogen, and may be fused to one or more additional rings,

wherein said complex is effective to catalyze the enantioselective alkylation of an allyl group bearing a leaving group at its allylic position.

2. The composition of claim 1, wherein said metal atom is molybdenum.

3. The composition of claim 1, wherein a single such ligand L^1 is coordinated to said metal atom.

4. The composition of claim 1, wherein said first and second chiral centers are further substituted with groups R^1 and R^2, respectively,

wherein R^1 and R^2 are independently selected from aryl, heteroaryl, aralkyl, carbocycle, or heterocycle, and are optionally substituted with one or more groups selected from alkyl, alkenyl, aryl, aralkyl, alkoxy, aryloxy, acyl, acyloxy, amide, tertiary amine, nitro, or halogen, or

R^1 and R^2 together form a carbocyclic or heterocyclic ring, which is optionally substituted with one or more groups selected from alkyl, alkenyl, aryl, aralkyl, alkoxy, aryloxy, acyl, acyloxy, amide, tertiary amine, nitro, or halogen, and which may be fused to one or more additional rings.

5. The composition of claim 4, wherein $R^1 = R^2$ = phenyl.

6. The composition of claim 4, wherein R^1 and R^2 form a 5- to 7- membered carbocyclic ring or a 5- to 7-membered heterocyclic ring having 3 to 6 carbon ring atoms and the remaining ring atoms selected from oxygen and nitrogen.

7. The composition of claim 1, wherein said chiral centers are connected by a direct bond or by a chain of one to three atoms comprising linkages selected from alkyl, alkyl ether, alkyl amino, or a combination thereof.

8. The composition of claim 7, wherein said chiral centers are connected by a direct bond, and said chiral component is thereby derived from a chiral 1,2-diol, -diamine, or -amino alcohol.

9. The composition of claim 8, wherein said chiral component is derived from a chiral 1,2-diamine.

10. The composition of claim 9, wherein said chiral 1,2-diamine is selected from 1R,2R-*trans*-diaminocyclohexane, 1R,2R-*trans*-diphenyl-1,2-ethanediamine, 3R,4R-*trans*-3,4-diamino-N-benzylpyrrolidine, 1R,2R-*trans*-diaminocycloheptane, 5R,6R-*trans*-5,6-diaminoindan, and the S,S-counterpart of any of the above.

11. The composition of claim 10, wherein said chiral 1,2-diamine is selected from 1R,2R-*trans*-diaminocyclohexane, 1R,2R-*trans*-diphenyl-1,2-ethanediamine, 1R,2R-*trans*-diaminocycloheptane, and the S,S-counterpart of any of the above.

12. The composition of claim 1, wherein said heterocyclic binding group Cy_N is a 5- to 7-membered ring having 1 to 6 carbon ring atoms, with the remaining ring atoms selected from oxygen and nitrogen.

13. The composition of claim 12, wherein said group Cy_N is a heteroaryl group.

14. The composition of claim 15, wherein said group Cy_N is a 2-pyridyl group.

15. The composition of claim 1, wherein said group Cy_N is linked, at a ring carbon atom adjacent said ring nitrogen atom, to said group X of said chiral component, via a carbonyl linkage.

16. The composition of claim 15, wherein said ligand L^1 is selected from N,N'-1R,2R-cyclohexanediylbis(2-pyridinecarboxamide), N,N'-1R,2R-1,2-diphenylethanediylbis(2-pyridinecarboxamide), N',N"-3R,4R-3,4-diamino-N-benzylpyrrolidinediylbis(2-pyridinecarboxamide), N,N'-1R,2R-cycloheptanediylbis(2-pyridinecarboxamide), N,N'-5R,6R-indandiylbis(2-pyridinecarboxamide, N,N'-1R,2R-cyclohexanediylbis(2-(6-methyl)pyridinecarboxamide), N,N'-1R,2R-cyclohexanediylbis(2-(4-nitro)pyridinecarboxamide), N,N'-1R,2R-cyclohexanediylbis(2-(4-methoxy)pyridinecarboxamide), and the S,S- counterpart of any of the above.

17. A catalytic organometallic composition, wherein the composition is the product of a process which comprises

contacting, in a suitable solvent, a chiral ligand L^1 comprising:

(i) a chiral component derived from a chiral diamine, diol, or amino alcohol, said component

having first and second chiral centers, each substituted with a group X selected from -O- or -NR-, where R is hydrogen or lower alkyl, and, linked to each said group X,

(ii) a binding group Cy_N comprising a heterocyclic group having a ring nitrogen atom effective to bind to said central metal atom, wherein said heterocyclic group is optionally substituted with one or more groups selected from alkyl, alkenyl, aryl, aralkyl, alkoxy, aryloxy, acyl, acyloxy, amide, tertiary amine, nitro, or halogen, and may be fused to one or more additional rings,

with a hexacoordinate complex of a metal selected from tungsten (0), chromium (0), and molybdenum(0),

whereby said complex undergoes a ligand exchange reaction, such that L^1 becomes coordinated to said metal atom;

wherein said composition is effective to catalyze the enantioselective alkylation of an allyl group bearing a leaving group at its allylic position.

18. The composition of claim 17, wherein in said process said metal is molybdenum (0).

19. The composition of claim 17, wherein in said process said hexacoordinate complex comprises ligands selected from the group consisting of CO, cycloheptatriene, lower alkyl nitrile, and lower alkyl isonitrile.

20. The composition of claim 17, wherein said first and second chiral centers are further substituted with groups R^1 and R^2, respectively,

wherein R^1 and R^2 are independently selected from aryl, heteroaryl, aralkyl, carbocycle, or heterocycle, and are optionally substituted with one or more groups selected from alkyl, alkenyl, aryl, aralkyl, alkoxy, aryloxy, acyl, acyloxy, amide, tertiary amine, nitro, or halogen, or

R^1 and R^2 together form a carbocyclic or heterocyclic ring, which is optionally substituted with one or more groups selected from alkyl, alkenyl, aryl, aralkyl, alkoxy, aryloxy, acyl, acyloxy, amide, tertiary amine, nitro, or halogen, and which may be fused to one or more additional rings.

21. The composition of claim 20, wherein said chiral centers are connected by a direct bond, and said chiral component is thereby derived from a chiral 1,2-diol, -diamine, or -amino alcohol.

22. The composition of claim 17, wherein said heterocyclic binding group Cy_N is a 5- to 7-embered ring having 1 to 6 carbon ring atoms, with the remaining ring atoms selected from oxygen and nitrogen.

23. The composition of claim 22, wherein said group Cy_N is a heteroaryl group.

24. A method of selective alkylation of an allyl group bearing a leaving group at the allylic position, said method comprising

reacting said allyl group with an alkylating agent in the presence of a catalytic amount of an alkylating catalyst, wherein said catalyst is an octahedral complex having a central metal atom selected from the group consisting of molybdenum, tungsten, and chromium, and coordinated thereto, a chiral ligand L^1, said ligand comprising

(i) a chiral component derived from a chiral diamine, diol, or amino alcohol, said component having first and second chiral centers, each substituted with a group X selected from -O- or -NR-, where R is hydrogen or lower alkyl, and, linked to each said group X,

(ii) a binding group Cy_N comprising a heterocyclic group having a ring nitrogen atom effective to bind to said central metal atom, wherein said heterocyclic group is optionally substituted with one or more groups selected from alkyl, alkenyl, aryl, aralkyl, alkoxy, aryloxy, acyl, acyloxy, amide, tertiary amine, nitro, or halogen, and may be fused to one or more additional rings,

under conditions effective to produce an alkylated product which is enriched in one of the possible isomeric products of such alkylation.

25. The method of claim 24, wherein said alkylation is enantioselective, and produces an alkylated product having an enantiomeric excess greater than 75%.

26. The method of claim 24, wherein said allyl group is nonsymmetrically substituted at its termini, and said alkylating is regioselective, such that said allyl group is alkylated at its more sterically hindered terminus.

27. The method of claim 26, wherein the regioselectivity of said alkylation, defined as the ratio of product alkylated at the more sterically hindered terminus of said allyl group to product alkylated at the less sterically hindered terminus of said allyl group, is greater than 3:1.

28. The method of claim 24, wherein said metal atom is molybdenum.

29. The method of claim 24, wherein said chiral component is derived from a chiral 1,2-diamine.

30. The method of claim 24, wherein said heterocyclic binding group Cy_N is a 5- to 7-membered ring having 1 to 6 carbon ring atoms, with the remaining ring atoms selected from oxygen and nitrogen.

31. The method of claim 30, wherein said group Cy_N is a heteroaryl group.

32. The method of claim 31, wherein said group Cy_N is a 2-pyridyl group.

33. The method of claim 24, wherein said group Cy_N is linked, at a ring carbon atom adjacent said ring nitrogen atom, to said group X of said chiral component, via a carbonyl linkage.

34. The method of claim 33, wherein said ligand L^1 is selected from N,N'-1R,2R-cyclohexanediylbis(2-pyridinecarboxamide), N,N'-1R,2R-1,2-diphenylethanediylbis(2-pyridinecarboxamide), N',N"-3R,4R-3,4-diamino-N-benzylpyrrolidinediylbis(2-pyridinecarboxamide), N,N'-1R,2R-cycloheptanediylbis(2-pyridinecarboxamide), N,N'-5R,6R-indandiylbis(2-pyridinecarboxamide), N,N'-1R,2R-cyclohexanediylbis(2-(6-methyl)pyridinecarboxamide), N,N'-1R,2R-cyclohexanediylbis(2-(4-nitro)pyridinecarboxamide), N,N'-1R,2R-cyclohexanediylbis(2-(4-methoxy)pyridinecarboxamide), and the S,S- counterpart of any of the above.

35. The method of claim 24, wherein neither terminus of said allyl group is aryl substituted.

36. The method of claim 35, wherein at least one terminus of said allyl group is substituted with an alkyl group.

37. The method of claim 35, wherein at least one terminus of said allyl group is substituted with a non-aromatic conjugated polyene or enyne.

38. The method of claim 24, wherein the allyl group has identical non-hydrogen substituents at its termini, with the exception of said leaving group, and said alkylation is enantioselective with respect to the new chiral center formed by said alkylation.

39. The method of claim 24, wherein the alkylating agent is a stabilized carbanion.

40. The method of claim 39, wherein the alkylating agent is of the form $EE'RC^- M^+$, where E and E' are electron-withdrawing substituents, and M^+ is a positively charged counterion.

41. The method of claim 40, where E and E' are independently selected from the group consisting of keto and carboxylic ester.

42. The method of claim 24, wherein said catalyst is formed *in situ* by ligand exchange of a soluble hexacoordinate molybdenum(0) complex with ligand L^1.

43. The method of claim 42, wherein said ligands are selected from the group consisting of CO, cycloheptatriene, lower alkyl nitrile, and lower alkyl isonitrile.

44. The method of claim 24, wherein the mole percent of said catalyst with respect to said substrate is from about 0.5% to about 15%.

45. The method of claim 44, wherein said mole percent is from about 1% to about 10%.

46. A method of selective alkylation of an allyl group bearing a leaving group at the allylic

position, said method comprising

reacting said substrate with an alkylating agent in the presence of a catalytic composition formed by contacting, in a suitable solvent, catalytic amounts of (i) a hexacoordinate complex of a metal selected from the group consisting of molybdenum (0), tungsten (0), and chromium (0) and (ii) a chiral ligand L^1, said ligand comprising

(i) a chiral component derived from a chiral diamine, diol, or amino alcohol, said component having first and second chiral centers, each substituted with a group X selected from -O- or -NR-, where R is hydrogen or lower alkyl, and, linked to each said group X,

(ii) a binding group Cy_N comprising a heterocyclic group having a ring nitrogen atom effective to bind to said central metal atom, wherein said heterocyclic group is optionally substituted with one or more groups selected from alkyl, alkenyl, aryl, aralkyl, alkoxy, aryloxy, acyl, acyloxy, amide, tertiary amine, nitro, or halogen, and may be fused to one or more additional rings,

under conditions effective to produce an alkylated product which is enriched in one of the possible isomeric products of such alkylation.

47. The method of claim 46, wherein said alkylation is enantioselective.

48. The method of claim 47, wherein said alkylation produces an alkylated product having an enantiomeric excess greater than 85%.

49. The method of claim 46, wherein said metal atom is molybdenum.

50. The method of claim 46, wherein said hexacoordinate complex comprises ligands which are effective to form a stable complex with said metal atom and which are displacable by ligand L^1 under the conditions of said ligand exchange.

51. The method of claim 50, wherein said ligands are selected from the group consisting of CO, cycloheptatriene, lower alkyl nitrile, and lower alkyl isonitrile.

52. The method of claim 46, wherein the mole percent of said catalytic composition with respect to said substrate is from about 0.5% to about 15%.